

# Thermodynamics of Solubility of Tri-*n*-butyl Phosphate in Nitric Acid Solutions

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## Abstract

The solubility of tri-*n*-butyl phosphate (TBP) in nitric acid of various concentrations (0 – 14 M) has been determined in the temperature range of 25 to 60°C. The concentrations of TBP dissolved in aqueous phase, both free and bound to the acid due to the formation of TBP complexes with nitric acid, have been calculated. A classical thermodynamic approach has been used to determine the formation constants of TBP-nitric acid complexes. The effect of temperature and the presence of heavy metal ions such as zirconium and ruthenium on the solubility of TBP in aqueous phase have also been analysed.

## Keywords

*Tri-butyl Phosphate Solubility; PUREX Process; Competitive Equilibria; Nuclear Fuel Reprocessing*

## Introduction

The most widely used PUREX process employs tri-butyl phosphate (TBP) diluted with hydrocarbon as an extractant for the recovery and purification of uranium and plutonium from the spent nuclear fuels. The aqueous streams (raffinate and product solutions) leaving the extraction cycles of this process contain small amount of TBP due to its mutual solubility with the aqueous phase. The aqueous solubility of tri-*n*-butyl phosphate is a concern for safety considerations in the reprocessing plants as it is potentially hydrolyzable to non-volatile species [Burger & Forcman (1951); Shulze & Navaratil (1984); Biplab et al. (2011)]. Removal of this dissolved TBP is of considerable interest in reprocessing process for the safe disposal of raffinate waste. The commonly used method for the removal of dissolved organics from the aqueous streams of PUREX process is diluent wash using suitable extraction equipment. Diluents like *n*-dodecane, normal paraffin hydrocarbon, kerosene etc. affect the solubility of TBP in the aqueous phase. It is therefore of fundamental importance to study the distribution equilibria of TBP between aqueous and organic phase (diluent). The equilibrium study will permit the estimation of amount of TBP in various concentrations of nitric acid, which will be useful in designing a suitable contactor.

A number of studies on solubility of TBP in aqueous solutions have been reported in the literature. Kuno et al. (1993) investigated the solubility of TBP in aqueous solutions of plutonium nitrate and in highly radioactive waste of PUREX process. They correlated solubility of TBP in plutonium nitrate solutions in the range of 0 ~ 0.1M and 1 ~ 8M by an empirical formula. Alcock et al. (1956) measured the mutual solubility of TBP and water system in presence of nitric acid and also in presence of various diluents like kerosene, benzene, toluene, hexane and cyclohexane. The solubility of TBP and its decomposition products in nitric acid containing uranyl nitrate in the concentration range 200-1200 g/L at 25-128°C has been reported by Usachev et al. (2004). Sagert & Lee (1980) have measured the distribution of lower trialkyl phosphate like trimethyl, triethyl, tripropyl and tri-butyl phosphate between water and dodecane as a function of temperature and trialkyl phosphate concentrations. Recently, Velavendan et al. (2012) have studied the effect of uranium and various fission product metal ion concentrations on the solubility of TBP in various nitric acid concentrations (0-15.7M) at room temperature. Although enough literature on solubility of pure TBP or TBP/diluents in aqueous medium have been reported, but literature on TBP solubility in presence of electrolytes in various nitric acid concentrations over a range of temperatures is incomplete and sometimes contradictory as well. Hence, it was found essential to generate solubility data for pure TBP and in different concentrations of nitric acid in the presence of different electrolytes as a function of temperature which has direct application to our reprocessing plant.

The solubility of nonelectrolytes in aqueous electrolyte solutions has traditionally been modeled by using the Setschenow equation for salt effect [Alcock et al. (1956); Higgins et al. (1959)]. Use of the Setschenow equation for aqueous solubility of TBP under limited conditions has been reported in the literature. Shekhar Kumar &

Koganti (2000) have proposed an empirical relation based on an extended salt effect model to predict the aqueous solubility of TBP in 5 to 100% TBP/*n*-dodecane-nitric acid-water biphasic system at 298.2 K. However, empirical correlations often used for this purpose cannot be considered reliable under conditions that are outside the experimental data base used to validate the model. There is no generalized model available to account for the presence of the diluent and for the case of multicomponent electrolyte solutions in which only some electrolytes are solvated and extracted by TBP. This paper presents the results on the thermodynamic modeling of the aqueous solubility of tri-*n*-butyl phosphate in nitric acid of various concentrations (0 – 14 M) which is an important parameter for safety considerations in the reprocessing of spent nuclear fuel by PUREX process.

## Experimental

All the reagents employed for the experiments were of analytical grade. Zirconium nitrate (GR, 99%, Merck) and ruthenium nitrosyl nitrate (AR, 1.7%, Arora Matthey) were used for the preparation of the required stock solutions. Double distilled water was used for dilutions and for preparing other aqueous standard solutions.

The solubility of tri-butyl phosphate in aqueous nitric acid solutions was measured at 25, 40 and 60°C. The experiments were performed in test-tubes with ground stoppers by shaking equal volumes of the aqueous and organic phases. The phases were brought into contact and then allowed to separate in water bath which controlled the temperature within  $\pm 0.5^\circ\text{C}$ . After phase separation, the aqueous phase was analysed for acid and tri-butyl phosphate.

The acidity of aqueous phase was estimated using titration with standardized sodium carbonate. The TBP content dissolved in the aqueous phase was determined by Gas chromatography method, details of which are described elsewhere [Pandey et al. (1998)].

## Results and discussion

In aqueous solutions of electrolyte, virtually non-extractable by TBP (such as  $\text{NaNO}_3$ ,  $\text{NaCl}$ ,  $\text{KCl}$  etc.) the solubility of the extractant decreases with increase in electrolyte concentration [Belousov & Zakharova (1975); Gordon (1975)]. The TBP soluble in the aqueous

phase will be only in the form of TBP molecules which are not combined with the electrolytes. Its solubility in such electrolyte solutions obeys the Setschenow equation [Setschenow (1899)] which is given by,

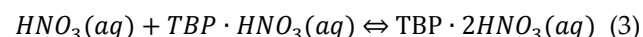
$$\log C_{TBP}^e = \log [TBP]_w - k_s C_{el}^e \quad (1)$$

where,  $C_{TBP}^e$  is the analytical concentration of TBP in electrolyte solution,  $[TBP]_w$  the analytical concentration of TBP in water,  $C_{el}^e$  the equilibrium concentration of the electrolyte in aqueous phase and  $k_s$  the salting out coefficient or Setschenow coefficient. On the other hand, in solutions of electrolytes which are extracted by TBP, more complex situation exists. In the case of TBP-nitric system tri-butyl phosphate dissolves in the aqueous phase not only as a result of the transition of its molecules into aqueous phase but also as a result of formation of complex by the acid with TBP. Since Eq. (1) presupposes the absence of chemical reaction between the organic solvent and the electrolyte, hence it is invalid in the above form for the electrolytes extractable by tri-butyl phosphate. In this case, Setschenow equation can be applied only to free tri-butyl phosphate i.e. not bound to the acid.

The complexation of nitric acid by TBP can be described on the basis of the following reaction equilibria:



and



Equation (2) is accounted for the extraction of nitric acid by TBP at higher acidities. The extraction data of Davis (1962), however, suggest that the 1:2 complex does not become the major TBP species until the aqueous  $\text{HNO}_3$  concentration reaches 8 to 10M. The equilibrium constants for Eqs (2) and (3) in terms of activities are,

$$K_1 = \frac{a_{\text{TBP} \cdot \text{HNO}_3}}{a_{\text{TBP}} \cdot a_{\text{HNO}_3}} \quad (4)$$

$$K_2 = \frac{a_{\text{TBP} \cdot 2\text{HNO}_3}}{a_{\text{TBP} \cdot \text{HNO}_3} \cdot a_{\text{HNO}_3}} = \frac{a_{\text{TBP} \cdot 2\text{HNO}_3}}{K_1 a_{\text{TBP}} a_{\text{HNO}_3}^2} \quad (5)$$

Representing organic phase activity in terms of products concentration and activity coefficients and separating the organic phase activity coefficients from the right side of Eqs, (4) and (5) gives,

$$K_1^* = K_1 \frac{\gamma_{\text{TBP}}}{\gamma_{\text{TBP} \cdot \text{HNO}_3}} = \frac{[\text{TBP} \cdot \text{HNO}_3]}{[\text{TBP}]_f \cdot a_{\text{HNO}_3}} \quad (6)$$

and

$$K_2^* = K_1 K_2 \frac{\gamma_{\text{TBP}}}{\gamma_{\text{TBP} \cdot 2\text{HNO}_3}} = \frac{[\text{TBP} \cdot 2\text{HNO}_3]}{[\text{TBP}]_f \cdot a_{\text{HNO}_3}^2} \quad (7)$$

where  $[TBP_f^e]$  is the equilibrium concentration of free TBP dissolved in the aqueous phase. Based on the extraction equilibria in Eqs (2) and (3), the total aqueous concentration of TBP bound to acid is given by,

$$[TBP]_{bound}^e = [TBP \cdot HNO_3] + [TBP \cdot 2HNO_3] \quad (8)$$

or,

$$[TBP]_{bound}^e = K_1^* [TBP_f^e] \cdot a_{HNO_3} + K_1^* \cdot K_2^* [TBP_f^e] \cdot a_{HNO_3}^2 \quad (9)$$

On dissolution of the tri-butyl phosphate not bound to the acid in the aqueous phase, the Setschenow equation holds in the form,

$$\log[TBP_f^e] = \log[TBP]_w - k_s C_{HNO_3}^e \quad (10)$$

Then, mass balance equation for TBP in the aqueous phase can be written as,

$$[TBP]_{bound}^e = C_{TBP}^e - [TBP_f^e] \quad (11)$$

Estimation of equilibrium constants of Eqs (6) and (7) requires values of activity of un-dissociated nitric acid which are obtained from the data reported by Davis & Bruin (1964) by correlating their results as functions of the stoichiometric aqueous nitric acid concentration. The degree of dissociation of nitric acid estimated by Davis and Bruin was correlated using the stoichiometric nitric concentrations in the aqueous phase as follows:

$$\ln(\alpha) = -3 \times 10^{-5} C_{HNO_3}^4 + 7 \times 10^{-4} C_{HNO_3}^3 - 0.0105 C_{HNO_3}^2 - 3.7 \times 10^{-3} C_{HNO_3} - 0.0039 \quad (12)$$

The activity of un-dissociated nitric acid was calculated from

$$a_{HNO_3} = \gamma_u C_u = \gamma_u (1 - \alpha) C_{HNO_3} \quad (13)$$

Similarly, activity coefficient of un-dissociated nitric acid was determined by least-square fitting using the experimental results of Davis & Bruin and expressed as follows:

$$\ln(\gamma_u) = -0.0019688 C_{HNO_3}^2 + 0.31034 C_{HNO_3} - 0.001482 \quad (14)$$

$$0.05 \leq C_{HNO_3} \leq 14M$$

TABLE 1 EQUILIBRIUM CONSTANTS AND SALTING OUT COEFFICIENT VALUES AT 25°C

Parameter	$K_1^*$	$K_2^*$	$k_s$
No metal ions	0.0092	0.0042	0.0765
In presence of zirconium	0.0047	0.006	0.0641
In presence of ruthenium	0.004	0.0104	0.0621

Equilibrium constants and salting coefficient were determined by non-linear regression analysis of experimental data by using Eqs. (10 – 14) and values are listed in Table 1. The solubility of TBP in various concentrations of nitric acid (0 to 14M) at different temperatures from 25 to 60°C in presence of ruthenium

and zirconium has been measured. Figures 1, 3, 5 and 6 show the comparison between experimental and calculated values of aqueous solubility of TBP and reasonably good agreements are achieved.

### Effect of Nitric Acid Concentration

Variation of aqueous solubility of TBP with nitric acid concentration is shown in Fig.1 at 25°C. It is observed that with increase in acidity solubility of TBP decreases slowly, passes through a minimum at about 8M and then increases with acidity.

The initial decrease in solubility of TBP with increasing acid concentration (up to about 8M) is probably due to the fact that in this region dissolution takes mainly as a result of the transition of free TBP molecules into the aqueous solution (i.e., physical solubility). The formation of compounds by the acid and TBP makes a small contribution to the solubility in this region.

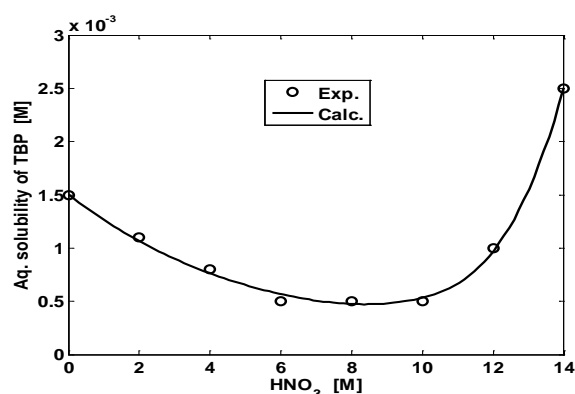


FIG. 1 AQUEOUS SOLUBILITY OF TBP AS A FUNCTION OF NITRIC ACID CONCENTRATION AT 25°C

With increase in acidity, the concentration of various TBP-nitric complex rises (as shown in Figs. 2(a) & (b)) and the solubility of TBP in the aqueous phase increases.

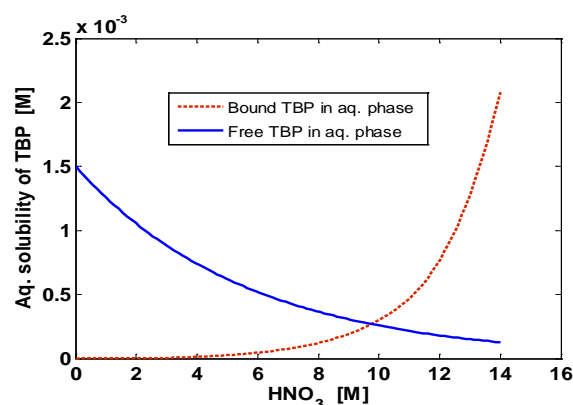


FIG.2 (A) CONC. OF BOUND TBP AND FREE TBP VS ACIDITY

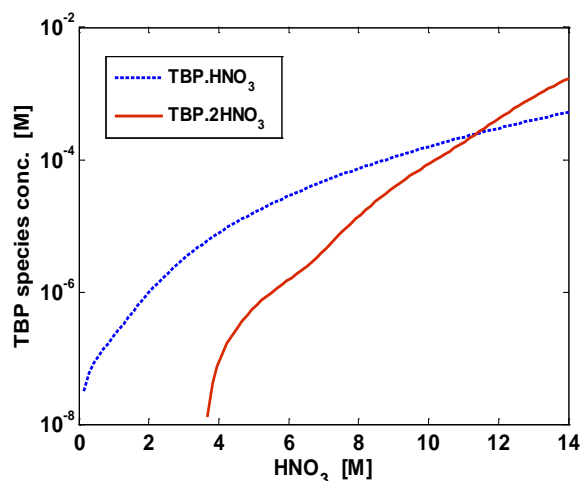


FIG.2 (B) CONC. OF DIFFERENT SPECIES OF TBP VS ACIDITY

### Effect of Temperature

Figure 3 presents a comparison between experimental and calculated values of aqueous phase solubility of 100% TBP at different temperatures and acidities. It is observed that with increase in temperature the solubility of TBP in aqueous phase increases.

There are discrepancies in the literature on solubility data as a function of temperature. Two studies report the solubility of TBP in the aqueous phase decreases with temperature [Higgins et al. (1959); Bolousov & Zakharova (1975)] but three others declare that with increase in temperature the solubility of TBP increases [Kuno et al (1993); Usachev & Markov (2003, 2004)]. Our results are in accordance with the data reported by Kuno et al (1993); Usachev & Markov (2003, 2004)

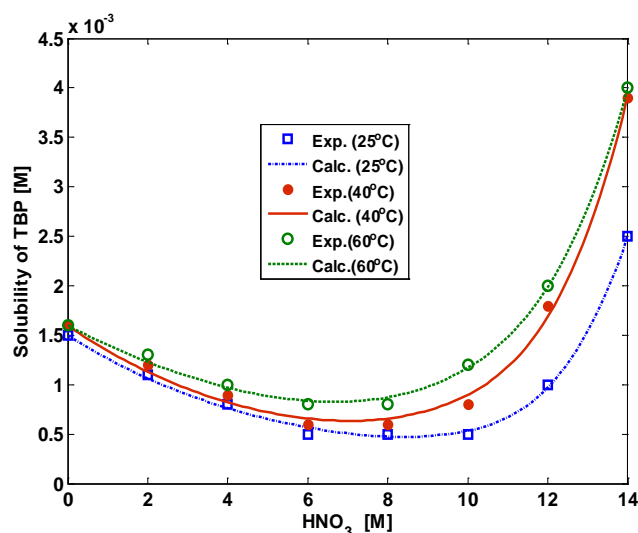


FIG.3. SOLUBILITY OF PURE TBP IN AQUEOUS PHASE AS A FUNCTION OF TEMPERATURE AND ACIDITY

The temperature dependency of the equilibrium constant of the reversible reaction is given by van't Hoff's relationship as,

$$\frac{d(\ln K)}{dT} = \frac{\Delta H}{RT^2} \quad (15)$$

If the enthalpy change of the reaction,  $\Delta H$  is assumed constant over the temperature range then, Eq. (15) can be easily integrated to give

$$\ln \frac{K}{K_1} = -\frac{\Delta H}{R} \left( \frac{1}{T} - \frac{1}{T_1} \right) \quad (16)$$

Figure 4 (a and b) show the plots of natural logarithm of equilibrium constants vs reciprocal of temperature and they are linear in agreement with Eq. (16). The values of  $\Delta H$  obtained from the slope of these plots using least-square fitting are given in Table 2. The values of free energy and entropy change were calculated using the following equations:

$$\Delta G = -RT \ln K \quad (17)$$

$$\Delta G = \Delta H - T\Delta S \quad (18)$$

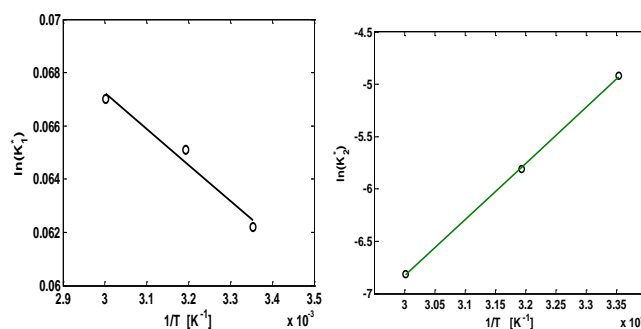


FIG. 4 EFFECT OF TEMPERATURE ON EQUILIBRIUM CONSTANTS

### Effect of Individual Metal Ions

Solubility of TBP in nitric solutions was measured in presence of Zr and Ru concentration of about 1 g/L separately and the comparison of experimental and calculated values is shown in Fig. 5.

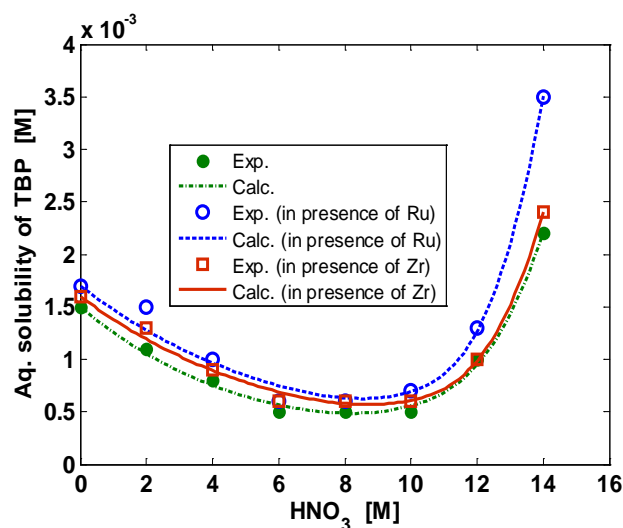


FIG. 5 EFFECT OF PRESENCE OF Zr AND Ru ON SOLUBILITY OF TBP AT DIFFERENT NITRIC ACID CONCENTRATIONS

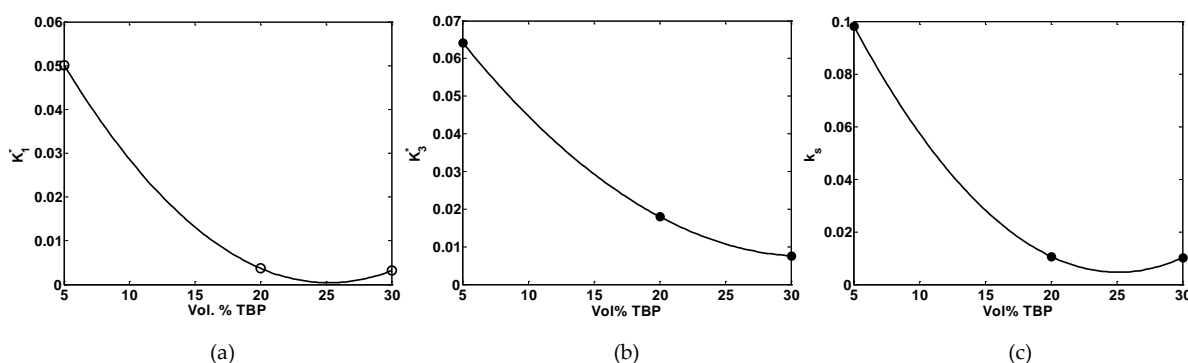


FIG. 7 VARIATION OF EQUILIBRIUM CONSTANT AND SALTING OUT COEFFICIENT WITH TBP CONCENTRATION

It is observed that the presence of these metals in aqueous solutions of nitric acid increases the solubility of TBP. In the presence of ruthenium ions, there is significant increase in solubility of TBP (as observed from Fig 5) as compared to that of zirconium ions. The solubility curve followed the same trend i.e., it falls gradually with increase in acidity, attains a minimum and again increases with rise in nitric acid concentration.

TABLE 2 VALUES OF THERMODYNAMIC PARAMETERS

Parameter	$\Delta H$ kCal/mol	$\Delta G$ kCal/mol	$\Delta S$ Cal / (mol. K)
For equation (2)	12.96	3.3	32.4
For equation (3)	-18.78	2.8	-72.5
For physical solubility	-0.42	1.8	-4.8

### Effect of TBP Concentration

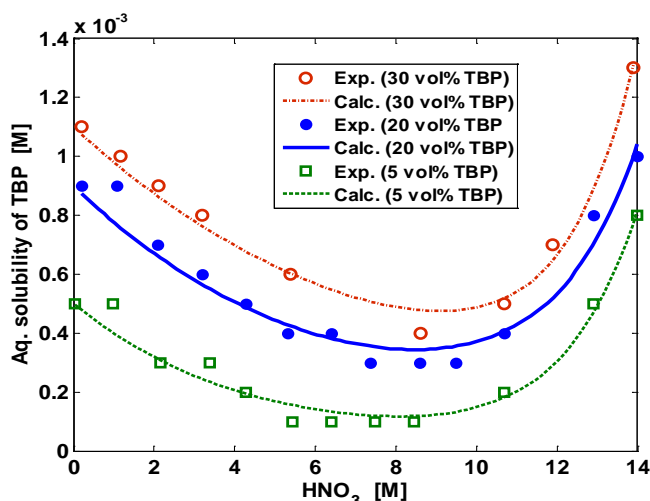


FIG. 6 EFFECT OF VOLUME PERCENT TBP ON SOLUBILITY OF TBP AT DIFFERENT NITRIC ACID CONCENTRATIONS

Figure 6 shows the comparison between experimental and calculated values of aqueous solubility of TBP at different volume percent of TBP as function of nitric acid concentrations. It is observed that solubility of TBP in aqueous nitric acid solutions decreases with volume percent of TBP. This may be due to the fact

that dissolution of TBP in aqueous phase is affected by the presence of a diluent as well the values of equilibrium constants and salting out coefficient are affected by the presence of diluent, just like in the case of extraction of uranium, plutonium etc. where distribution coefficients of these elements are functions of TBP concentration.

Figures 7 (a, b and c) show variation of equilibrium constants and salting out coefficient values with TBP concentrations. The equilibrium constants and salting out coefficient are correlated as a function of TBP concentrations as follows;

$$K_1^* = 0.6402F^{-1.624} \quad (19)$$

$$K_2^* = 0.41062F^{-1.121} \quad (20)$$

$$k_s = 0.80912F^{-1.35} \quad (21)$$

### Conclusions

The solubility of tributyl phosphate in nitric acid solutions (0–14M) has been measured at temperatures ranging from 25 to 60°C. The solubility data have been correlated using classical thermodynamic approach. The effect of temperature and presence of extractable salts like ruthenium and zirconium nitrate have been analysed using the model equations. With increase in temperature and in the presence of extractable salts the solubility of TBP in nitric acid increases. The agreement between experimental and calculated results are reasonably good. The thermodynamic parameters such as heat of reaction, free energy change and entropy change have also been estimated by analyzing the experimental data.

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